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Conductivity Change During Replacement of Na^+ by
Ag^+ in Polycrystalline Beta'' Alumina

by

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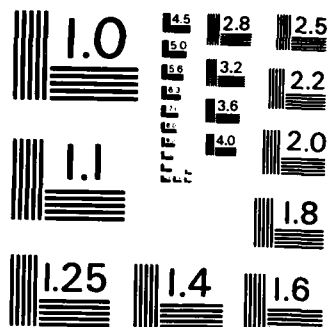
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The logitudal conductivity was determined by a four-probe technique during the replacement of Na^+ ions by Ag^+-ions from the inside of a closed-end tube. Similarly, the radial conductivity was measured during exchange starting from the outside. The conductivity-time curves display a minimum in conductivity when ion exchange time is steeper than that predicted by various models. The effects likely to produce additional resistances are presented.

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CONDUCTIVITY CHANGE DURING THE REPLACEMENT OF Na$^+$ IONS BY Ag$^+$ IONS IN POLYCRYSTALLINE BETA" ALUMINA

Manfred BREITER and Martha MALY-SCHREIBER* and Bruce DUNN**

The longitudal conductivity was determined by a four-probe technique during the replacement of Na$^{(+)}$ ions by Ag$^+$ ions from the inside of a closed-end tube. Similary, the radial conductivity was measured during exchange starting from the outside. The conductivity-time curves display a minimum with a conductivity value below that of the Ag B" alumina. The results also show that the change in conductivity with ion exchange time is steeper than that predicted by various models. The effects likely to produce additional resistances are presented.

1. INTRODUCTION

The ion exchange properties of β and β" aluminas have been rather well investigated[1,2]. Most of these studies involve single crystal materials where the sodium content has been completely replaced by another mobile ion. The properties of partially exchanged β and β" compositions have been studied to a much lesser extent. One of the more interesting features of these materials is the presence of a mixed alkali effect[3,5]. That is, when two mobile ions are present, intermediate compositions possess a lower conductivity (and higher activation energy for conduction) than either of the pure compositions. The effect has been reported for β and β" aluminates and gallates[4,5].

The studies involving partially exchanged materials generally utilize equilibrated samples which do not possess composition gradients. As a result, very little information is generated concerning the nature of the ion exchange process. A previous study by Breiter and Farrington[6] indicated that the kinetics of Ag$^+$ exchange in β alumina were significantly affected by the presence of grain boundaries. The present paper extends this work to polycrystalline β" alumina. In this case we use transport measurements to monitor the ion exchange process.

The result is that we are able to gain insight concerning the contributions of mixed alkali effects and interdiffusion processes on the ion exchange behaviour of polycrystalline beta" alumina.

2. EXPERIMENTAL

Cylinders (2.5 cm in length and about 1 cm in diameter) were cut from polycrystalline tubes of beta" alumina supplied by Ceramatec Inc. An alpha alumina cap was glass sealed to one end of the cylinder, thus producing a small cell with one open end. Photographs of such cells were already shown in Figure 1 of reference 7. By sealing the cylinder prior to ion exchange, discoloration effects are avoided.

Two types of ion exchange experiments were performed. In the first type, four narrow rings of silver paint were initially brushed onto the outside surface of the beta" alumina cylinder. The distance between these rings was approximately 0.5 cm. Four loops of thin silver wire were attached to the silver painted regions. The wires contacted the silver paint and were tightly held in place by two segments of an alpha alumina tube. Conductivity was measured by a four probe technique, using the silver wire loops as electrodes. This particular con-

figuration evaluates the longitudinal conductivity of the polycrystalline beta" alumina (i.e. along the major axis of the cylinder). A more detailed discussion of the measurement method was presented previously[8]. The impedance at 1000 Hz was essentially ohmic and the data shown in Figure 1 were obtained at this frequency.

The ion exchange and conductivity measurements were made in a small furnace which was heated by a DC current in order to reduce the noise level. The inside of the furnace was continuously flushed by a steady stream of nitrogen. Ag^+ exchange was accomplished by adding approximately 1.5 ml of molten $AgNO_3$ to the interior of the cell using a small pipette. This process constituted "inside" exchange and was periodically interrupted for the (longitudinal) conductivity measurements. The nominal temperature for the ion exchange and conductivity experiments was 295°C. It was necessary to remove the molten $AgNO_3$ prior to the conductivity measurement because of co-conduction through the molten salt. After the measurement, a fresh volume of $AgNO_3$ was added and a new period of conversion commenced. The total ion exchange time was determined by summing the individual conversion periods.

The second type of experiment involved ion exchange from the outside surface. The cell was placed in a bath of molten $AgNO_3$ at 295°C and care was taken to prevent the salt from reaching the inside surface. In this case a radial resistance measurement was employed. The interior of the beta" alumina cylinder was covered by silver paint and contact was made by a tightly fitting spiral of thick (~1 mm diameter) silver wire. The resistance was measured between a large cylinder of silver foil in the molten salt and the interior silver wire. The electrolytic resistance between the foil cylinder and the outer surface of the β" alumina tube was negligible compared to that of the solid electrolyte. There were no co-conduction paths and the transport measurements were made while the sample

was in the ion exchange bath. Once again the impedance was essentially ohmic over a wide frequency range and the impedance at 1000 Hz were used in Figure 1.

Gravimetric methods were employed to obtain a quantitative measure of the rate of ion exchange. For these experiments, the interior of a separate witness cell was filled with molten $AgNO_3$ and allowed to exchange. After a given period of time, the molten salt was removed by pipette and the cell taken from the furnace. It was repeatedly washed (distilled water and conc. HNO_3) and then dried for several hours at 200°C. The extent of ion exchange was obtained from the following relation

$$n_{ex} = 36.51 \left(\frac{W}{W_{in}} - 1\right) \tag{1}$$

where W is the weight of the sample at time, t, W_{in} is the initial weight of the sample and n_{ex} represents the amount of Na_2O (in weight %) replaced by Ag_2O. Both W and W_{in} were corrected for the additional weight provided by the cap and glass seal. The extent of ion exchange as a function of time was determined only for the "inside" exchange configuration. However, considering the dimensions of the sample, it may be expected that ion exchange from the outside would lead to similar results.

3. RESULTS

Figure 1 compares the conductivity values for the two types of exchange as a function of ion exchange time. Curve 3 reflects the data for exchange from the inside surface (i.e., longitudinal conductivity) while curve 4 gives radial conductivity results for ion exchange from the outside surface. Curves 1 and 2 were derived from the ion exchange models discussed in the next section. The original data for curve 3 were corrected for temperature fluctuations of ± 10 % which arose from removal of the molten $AgNO_3$ prior to measurement. These corrections

which amounted to less than 5 % were made by using the activation energy for conduction to obtain values at 295°C.
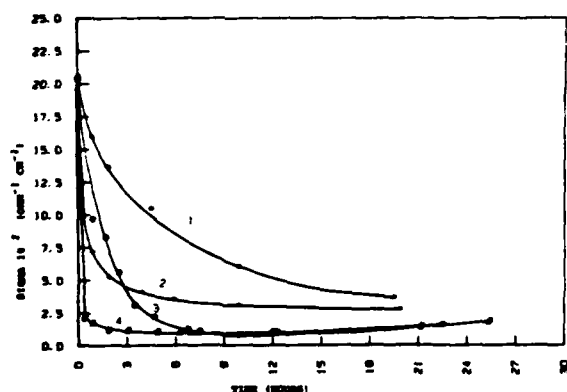

FIGURE 1
Conductivity as a function of exchange time in polycrystalline β" alumina at 295°C.
Curve 1:   longitudinal configuration - calcu-
           lated from Equation 2
Curve 2:   radial configuration - calculated
           from Equation 3
Curve 3:   inside exchange, longitudinal con-
           ductivity
Curve 4:   outside exchange, radial conductivity

Both curves 3 and 4 display qualitatively similar behaviour. The conductivity decreases from the initial value for Na^+ β" alumina and passes through a minimum conductivity. This minimum is rather shallow and much less pro-nounced than the types usually shown for mixed alkali effects[4,5]. After the minimum value (exchange ~ 12 hours), the conductivity increases slowly with ion exchange time and approaches the value for Ag^+ β" alumina. Although curves 3 and 4 exhibit distinctly different responses during the initial 8 hours, their conductivities practically coincide thereafter, including the region containing the minimum.

The time dependence of the Na^+ to Ag^+ exchange process is shown in Figure 2. The data were ob-tained from inside exchange experiments, and the time represents the cumulative time during which the interior of the cell was filled with mol-

ten $AgNO_3$. The behaviour of the β" alumina is comparable to that previously observed for β alumina, with the exception that ion exchange is considerably more rapid in β" alumina. It is important to note that in the prior work with β alumina, grain boundaries were found to be instrumental in the ion exchange process, exerting a retarding effect on the ion exchange kinetics[6].
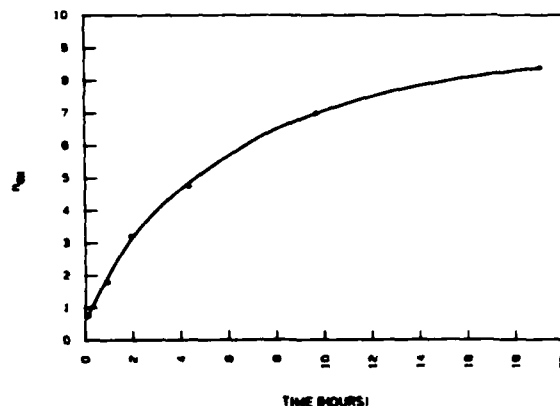

FIGURE 2
Exchanged sodium content (wt. %) as a function of time: inside exchange using $AgNO_3$ at 295°C.

4. DISCUSSION

The experimental results show two interesting features which warrant further discussion: (1) the different transport properties for the in-side and outside exchanged materials at short ion exchange times; and (2) the existence of a conductivity minimum at intermediate composi-tions of Na^+ and Ag^+. Although we have reason-able qualitative understanding of why these effects occur, rigorous models have not yet been developed.

The outside exchanged samples (curve 4 in Figure 1) exhibit a far more rapid decrease in conductivity than the inside exchanged material (curve 3). This behaviour arises from the spec-fic conductivity measurement methods and not fr any ion exchange anomalies. Radial conductivi-ties were obtained in the outside exchange wher as longitudinal conductivities were determined

for the inside exchange. At the short exchange times, each sample can be expected to consist of three distinct regions: an exchanged region which is predominantly Ag^+, an unexchanged region which is predominantly Na^+, and a mixed composition region. For the radial measurements, these three regions are connected in series. Since $\sigma_{Ag^+\beta"} < \sigma_{Na^+\beta"}$ the exchanged part contributes rather substantially to the total resistance, even at short exchange periods. In contrast, these three regions are connected in parallel when longitudinal conductivity is measured. Thus, the relative contribution of the exchanged section is correspondingly less. A larger amount of exchange is necessary before the longitudinal conductivity decreases to levels comparable to the short time values for radial conductivity. The difference between radial and longitudinal measurements was previously observed in hydration studies of sodium β and $\beta"$ alumina[8].

We have attempted to model this behaviour by using various mixing relationships. These modeling approaches are based on the assumption that the exchange region moves as a constant wave front through the wall of the $\beta"$ alumina cylinder. Thus, there are either exchanged regions (with conductivity σ_{Ag}) or unexchanged regions (with conductivity σ_{Na}). The resulting equations for longitudinal conductivity (inside exchange) are:

$$\sigma = \sigma_{Ag}\alpha + \sigma_{Na}(1-\alpha) \qquad (2)$$

with

$$\alpha = n_{ex}/8.85 \qquad (3)$$

where n_{ex} is defined by Equation (1) and 8.85 represents the initial Na_2O content of the sample. In this case the two sections are electrically in parallel. For radial conductivity (outside exchange) the two sections are in series and

$$\frac{1}{\sigma} = (\frac{1}{\sigma_{Ag}}\ln\frac{r_0}{r_\alpha} + \frac{1}{\sigma_{Na}}\ln\frac{r_\alpha}{r_i})\frac{1}{\ln r_0/r_i} \qquad (4)$$

Here r_0, r_α and r_i designate the outer radius,

the radius of the wave front and the inner radius.

Curves (1) and (2) reflect Equations (2) and (4), respectively. Although both curves display the proper trends (both conductivities decrease with time, radial being much steeper than longitudinal), neither curve constitutes a good fit to the data (see Figure 1). It is also significant to note that neither of the models are able to show the conductivity minimum observed in the experimental results.

Although the simple models demonstrate qualitative agreement, it is apparent that two limitations exist: the inability to predict either the short exchange time conductivity changes or the conductivity minimum. The latter is probably an artifact of the mixed alkali effect. The location of the minimum (~75 % Ag^+ exchange is similar to that reported by Wasiucionek et al.[5] in that the minimum occurs with Ag-rich compositions and at comparable percentages. At 295°C it is not surprising that the observed minimum is shallow. There is evidence that above 200°C the mixed alkali effect disappears for Na^+-$Ag^+\beta"$ alumina[5]. However, it is important to note that the present investigation offers far greater resolution of the conductivity values with much data coming from a region (i.e. at the minimum) which was not fully explored in the prior work.

The second important consideration is that the present experiments involve a non-euqilibrium distribution of the two cations. At this time it is not precisely clear how this non-equilibrium distribution might result in a conductivity decrease beyond that which is expected from the models. However, previous work by Yao and Kummer[1] does offer significant insights. These investigators found that the interdiffusion coefficient for alkali and silver cations in β alumina was less than that of the ion with the lowest self-diffusion coefficient.

That is, in Na^+-Ag^+ß alumina, the interdiffusion coefficient for Ag^+ was much less than the self-diffusion coefficient of Ag^+. If a similar effect occurs within the ß" alumina structure, it would give rise to an additional resistance and bring the models into better agreement with the observed behaviour, particularly at the short exchange times. Current studies are directed at establishing this interdiffusion effect.

5. CONCLUSIONS

We have used conductivity measurements to investigate the ion exchange behaviour of Na^+-Ag^+ polycrystalline ß" alumina. The inability of simple diffusion and mixing models to explain the experimental results suggests that more complex phenomena are involved. Two likely factors are the mixed alkali effect and interdiffusion processes, although a quantitative assessment of these items has yet to be developed. In both cases there is also the question of how grain boundaries influence these effects.

The experimental work clearly indicates that the distribution of the ion exchanged species is of central importance. As a result, a relatively small amount of ion exchange can exert a large influence on the conductivity. In radial measurements, the replacement of only 20 % $Na^{(+)}$ is able to cause conductivity values representative of Ag^+ß" alumina. This behaviour is quite significant for battery applications where cell resistance is measured in the radial direction. The exchange effect is not nearly as dramatic for the longitudinal configuration. In this case parallel resistance paths are available and nearly 50 % exchange is necessary before the conductivity of Ag^+ß" alumina is attained.

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